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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Lasers	Energy transfer
Chemical reactions	Reaction rates
Molecular collisions	Reagents
Excitation	Vibrational relaxation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The purpose of this research has been to determine the effect of selective electronic and vibrational excitation on energy transfer and reaction rates in simple molecular systems. The combined use of selective excitation and final state resolution has demonstrated that a broad variety of behavior is exhibited in collisions of simple chemical species. The principal results can be grouped into three sets (1) Influence of Reagent Energy on Chemical Reactions, (2) Vibrational Relaxation vs Reaction, and (3) Vibrational Relaxation in Polyatomic Systems.

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FINAL REPORT

ARO PROPOSAL NUMBER: RDRD-P-12224

PERIOD COVERED BY REPORT: April 1, 1974 - Sept. 30, 1977

TITLE OF PROPOSAL: Laser Studies of Molecular Collision Processes

CONTRACT OR GRANT NUMBER: DAHCO4 74 G 0148

NAME OF INSTITUTION: Department of Chemistry
University of California,
Berkeley, CA 94720

PRINCIPAL INVESTIGATOR: Professor C. Bradley Moore

I. Statement of Problem:

The purpose of this research has been to determine the effect of selective electronic and vibrational excitation on energy transfer and reaction rates in simple molecular systems.

II. Principal Results:

The combined use of selective excitation and final state resolution has demonstrated that a broad variety of behavior is exhibited in collisions of simple chemical species. The principal results can be grouped into three sets.

1) Influence of Reagent Energy on Chemical Reactions:

The type as well as the amount of excitation determines the outcome of chemical reactions. Electronic excitation generally allows the reaction to occur on several potential energy surfaces. In the case of the reaction of $Br(^2P_{1/2})$ + HI the spin orbit energy places the reaction on a surface on which the reaction is inhibited. In an extensive study of the temperature dependence, hot atom effects, and isotopic subsitution on the reactions of the X + HY type it is apparent that thermal

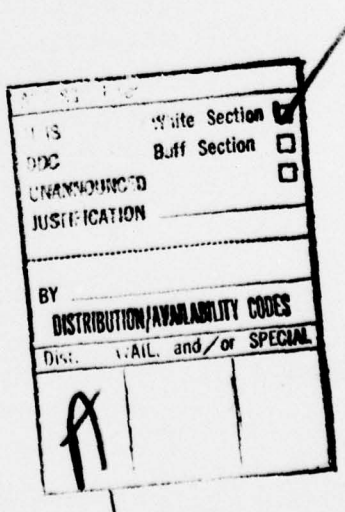
energy accelerates the reaction more efficiently than just translational energy. Vibrational energy accelerates both endothermic and exothermic reactions.

2) Vibrational Relaxation vs Reaction:

The collisions of vibrationally excited HCl(v = 1, 2) with O, Cl, Br, and H atoms have been studied. Vibration to translation and rotation energy transfer (V→ T, R) is very fast in these open-shelled, "chemically interacting" systems. The effect of additional vibrational quanta accelerate both reaction and deactivation. Two additional quanta accelerate the O + HCl reaction by a factor of 10^4. The relative branching into reactive vs relaxation seems to be system specific. Relaxation of HCl(v = 2) occurs four of five times faster than relaxation of HCl(v = 1).

3) Vibrational Relaxation in Polyatomic Systems:

Vibrational relaxation of diatomic molecules has been extensively studied and the general trends have been firmly established experimentally. In polyatomic systems the experiment is much harder due to reduced oscillator strengths and increased number of possible channels. The relaxation paths for vibrationally excited CH_4, H_2O, CO_2, and N_2O have been studied. In the case of H_2O very fast V → T, R processes and faster relaxation in the lower states than in the upper states have been observed.



III. Publications:

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